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Enhancement of tribological properties of 9Cr18 stainless steel by dual Mo and S Co implantation

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Mo and S ions were simultaneously implanted into 9Cr18 stainless steel samples. The frictional properties of the implanted samples were assessed using a pin-on-disk tester and the elemental depth profiles were measured by Auger electron spectroscopy. The hardness of the samples was also measured. We find that this dual-element implantation process reduces the coefficient of friction by a factor of 2 and increases the low-friction lifetime by a factor of 4 compared to the 9Cr18 surface with Mo or S implantation alone. This enhancement is related to the synergistic coexistence of the implanted elements at the same place. We have also investigated the process using computer simulation. The simulation results help disclose the characteristics of the modified layer and explain the effects of dual-element ion implantation.
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I. INTRODUCTION

MoS_2 is an excellent solid lubricant and is widely used in the space and vacuum industries to reduce the friction coefficient. Sputter deposition is the most common technique used to form MoS_2 lubricant films on workpiece surfaces. However, due to the considerable difference of the Young's modulus between the substrate and MoS_2 film, the film is liable to peel off under stress. Deposition of MoS_2 films with good adhesion and thickness uniformity can be a challenge. Fabrication of MoS_2 thin films by ion beams has been investigated by a number of workers.[1–3] Ag, Mo, and Au ion implantation has been shown to improve the density of MoS_2 films and to prolong the lifetime of the films.[4] N, Ti, and Mo ion implantation has been reported to decrease the friction coefficient of 9Cr18 stainless steel, enabling the 9Cr18 substrate to retain acceptable frictional properties even after the superficial MoS_2 film has peeled off.[5] In this article, we report our work on the coimplantation of Mo and S ions into 9Cr18 stainless steel. The influence of the Mo:S ratio in the Mo+S ion beam on the 9Cr18 frictional and hardness properties was investigated. A computer simulation program was developed and used to predict the compositional profile in the implanted layer.

II. EXPERIMENT

Ion implantation was conducted using a TITAN ion implanter which has been described elsewhere.[6] 9Cr18 stainless steel samples in the form of disks with a diameter of 45 mm and a thickness of 8 mm were polished to a mirror finish, followed by an ultrasonic clean. Three kinds of ion beams with atomic ratios Mo:S=1:0, 1:2, and 0:1 were used in our implantation experiments, formed from the TITAN vacuum arc ion source. A pure Mo cathode yielded an ion beam consisting of only Mo, that is, Mo:S=1:0. A cathode made of Mo and S with an atomic ratio of Mo:S=1:2 was employed to generate the Mo+S ion beam with Mo:S=1:2. Sulfur is an insulator and cannot produce a cathodic arc plasma directly. Thus, the S ion implantation was achieved using a cathode made of 9Cr18 and S with an atomic ratio of Fe+Cr:S=1:1.5. The resulting Mo:S ratio in the ion beam was 0:1. The Mo+S and S cathodes were made by compressing metal and S powders in a metal tube made of 9Cr18 stainless steel, and there were residual Fe and Cr in the cathode materials. The Mo+S and S ion doses were estimated according to the contents of Mo and S in the cathodes. The time-average ion beam current was less than $0.04\,mA/cm^2$ for all the ion implantation processes. The implantation parameters are displayed in Table I.

The elemental depth profiles were acquired using a SIA100 Auger analyzer. Friction tests were conducted using a pin-on-disk tester under a load of 5 N with a rotational speed of 3 rpm and a ruby ball with a diameter of 5 mm. The test was terminated when the friction coefficient reached 0.4. The friction coefficient f was determined by the steady-state value before the end of the test. An HRC hardness tester and DMH microhardness tester were used to measure the HRC and HK hardness of the samples. The HK hardness was measured with a load of 2 g. Each hardness value is the mean of at least three individual measurements.

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TABLE I. Ion implantation conditions.

Ion beam	Dose ($\times 10^{17}$ ions/cm^2)	Accelerating voltage (kV)
Mo	1	40
S	1	40
Mo+S	1, 2, 3	40

III. RESULTS AND DISCUSSION

The results of the hardness test of the samples are listed in Table II. The unimplanted sample has the highest HRC and HK values, and so the ion implantation process decreases both the HRC and HK values of the samples. The measured friction coefficients are shown in Table III. Mo or S implantation alone improves the friction properties only marginally. On the other hand, Mo+S coimplantation improves the friction properties significantly, with the 3×10^{17} ions cm^{-2} Mo+S implanted sample showing the lowest friction coefficient and longest lifetime (number of cycles before the friction coefficient increases precipitously). The x-ray ray diffraction (XRD) data acquired from the Mo+S implanted samples show no evidence of MoS_2 in the implanted layer. Since the measured Mo and S depth profiles coincide with each other very well in the Mo+S implanted sample (Fig. 1), it appears that the synergistic coexistence of Mo and S, without molecular MoS_2 formation, is sufficient to yield the superior frictional characteristics.

The observed Mo projected range is about 26 nm in the 1×10^{17} ions cm^{-2} Mo+S implanted sample. A Mo cathodic arc plasma has a mean charge state of 3.1.[7] The Mo projected range is consistent with a TRIM calculation with a Mo energy of $40\times3.1=124$ keV. The range of the S ions is about 24 nm. This distance corresponds to a S ion energy of 45 keV according to TRIM. Hence, it is roughly estimated that the S plasma has a mean charge state of $45/40>1$. These data thus indicate that the S plasma includes ions with 2+ or higher charge states.

The C and O contents are much higher than the Mo and S contents in the subsurface layer (20–30 nm under the surface) in all of the implanted samples. The Fe content in the subsurface layer is mainly influenced by the presence of C and O. The Fe content in the subsurface layer is about 50–60 at. % in all the implanted samples. As aforementioned, Fe and Cr ions exist in the Mo+S and S ion beams. The frictional properties of the Mo+S ion implanted samples are much better than those of the S ion implanted samples, whereas the frictional properties of the S ion implanted samples are similar to those of the Mo ion implanted samples. Considering that there are no Fe and Cr ions in the Mo ion beam, it can be inferred that Fe and Cr ion implantation has little influence on the frictional properties of the samples.

The results obtained in our experiments and by other research groups[1,8,9] show that the coincidence of the implanted elemental distributions is important for the improvement of the frictional properties of the sample in a dual-element ion implantation process. We define three parameters to characterize the coincidence of the implanted ion depth profiles. The first one is $F=f_1(x)f_2(x)$, where $f_1(x)$ and $f_2(x)$ are the concentration depth profiles of each implanted ion species in the implanted layer. The second one is $F_{\max}$, which is the maximum of F in the layer. The third one is T_C, the layer thickness for which both $f_1(x)$ and $f_2(x)>C$ in the implanted layer. C is the critical concentration of the implanted element in the sample above which the frictional properties are improved significantly. F reflects the coincident intensity of the depth profiles of the two implanted elements. By calculating $F_{\max}$, the maximum value of F in the implanted layer can be specified. Also, we can use $F_{\max}$ to compare the coincident intensity of the elemental depth profiles in different samples. T_C represents the effective coincidence range of the two depth profiles.

It is meaningful to describe this multicomponent ion implantation by computer simulation utilizing these three parameters.[6] In this program developed in our laboratories and based on the TRIM code, alternating implantation of two elements is used to simulate the simultaneous and continuous multicomponent ion implantation. Sputtering and composition changes in the target are also taken into account to make the program suitable for high-dose implantation. The target is divided into many thin layers so that the depth profile can be depicted with enough resolution. Each implanted ion or recoiled atom is traced to determine its final position and in which layer it has relocated to, and then the composition of each layer is adjusted during the simulation process accordingly. The particle numbers in the first layer (surface layer) and sometimes those in the second layer are altered on account of sputtering in addition to the ion implantation and recoiling processes. When all the particles in the surface layer are sputtered away, the second layer becomes the first layer and the indices of the other layers are subsequently changed. The simultaneous and continuous Mo+S ion implantation is treated as alternating processes of small-dose Mo ion implantation and small-dose S ion implantation. The cycles of Mo and S ion implantation are repeated until the final dose has been attained. The ion energies are determined by the average charge states. The ratio of the implanted ion doses is determined by the composition of the cathode, and

TABLE II. Hardness of the samples.

	Unimplanted	Mo implanted	S implanted	Mo+S 1×10^{17}	Mo+S 2×10^{17}	Mo+S 3×10^{17}
HRC	61.7	57.4	58.7	58.1	56.3	56.8
HK (kg mm^{-2})	947	865	881	850	839	823

TABLE III. Friction test results.

Sample (9Cr18)	Friction coefficient (F)	Lifetime (No. cycles)
unimplanted	0.28	950
1×10^{17} ions/cm^2 Mo+S implantation	0.13	2100
2×10^{17} ions/cm^2 Mo+S implantation	0.11	3500
3×10^{17} ions/cm^2 Mo+S implantation	0.11	4100
1×10^{17} ions/cm^2 S implantation	0.19	1300
1×10^{17} ions/cm^2 Mo implantation	0.20	1400

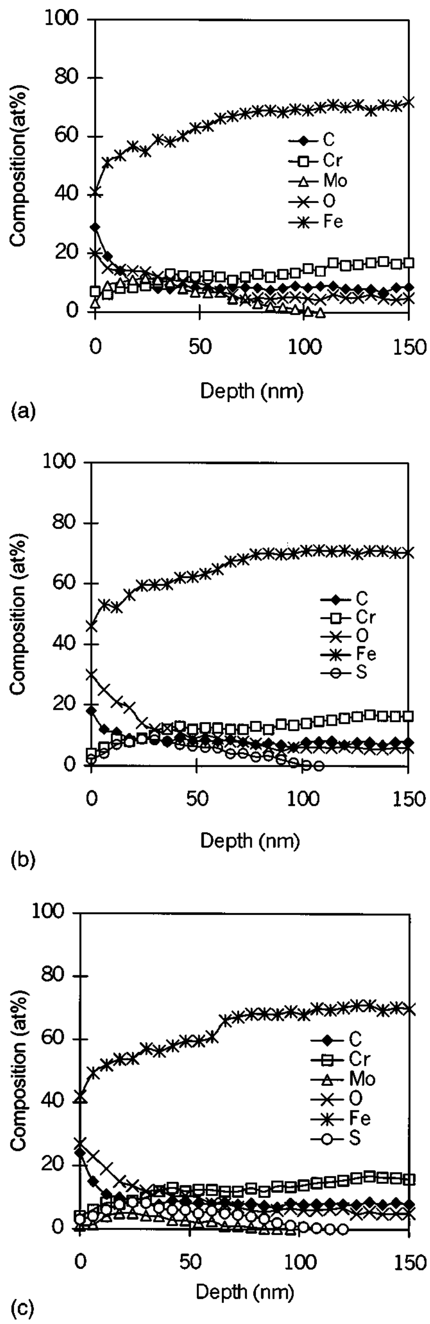

FIG. 1. Elemental depth profiles of the implanted samples obtained by Auger depth profiling: (a) Mo ion implanted sample; (b) S ion implanted sample; (c) Mo+S ion implanted sample. The dose is $1\times10^{17}\,\mathrm{cm}^{-2}$ and the accelerating voltage is 40 kV.

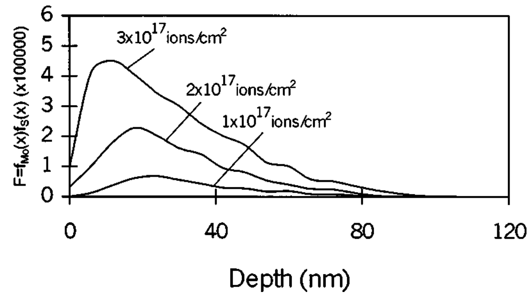

FIG. 2. Computer simulation results of $F=f_{\mathrm{Mo}}(x)f_{\mathrm{S}}(x)$. The implanted ions are Mo+S with the Mo:S ratio equal to 1:2. The dose of $1\times10^{17}\,\mathrm{cm}^{-2}$ corresponds to 4800 pseudoparticles. The accelerating voltage is 40 kV.

Fe and Cr ion implantation is neglected in the simulation. The fundamental model taking into account the penetration, sputtering, and collisional cascade of the incident ions in the target as well as the main modeling parameters are described elsewhere.[10]

Our simulation shows that $F=f_{\mathrm{Mo}}(x)f_{\mathrm{S}}(x)$ and $F_{\max}$ increase with higher implantation dose (Fig. 2). This indicates that simultaneous Mo+S ion implantation can give good coincidence of the Mo and S species. The $F_{\max}$ location moves towards the surface as the dose increases due to sputtering.

Noticing the evident rise in the lifetime of the sample implanted with 10^{17} Mo+S cm^{-2} over the unimplanted sample, as exhibited in Fig. 3, we conservatively determine C by setting $T_C=0$ in the Auger elemental depth profile of the sample implanted with $1\times10^{17}\,\mathrm{ions\,cm}^{-2}$ Mo+S ions (Fig. 1), yielding $C=0.06$. The T_C value can be calculated with $C=0.06$ (Fig. 4). The $T_{0.06}$ value, that is, the thickness of the effective modified layer in the implanted sample, clearly increases with increasing implant dose. Therefore, the larger the value of $T_{0.06}$, the better are the frictional characteristics. Through simulation, we can readily determine at what dose and energy the required performance of the implanted layer can be realized.

IV. CONCLUSION

Our study shows that simultaneous Mo and S coimplantation produces significantly better improvement in the frictional properties of 9Cr18 stainless steel than Mo or S implantation alone. Since XRD does not detect the existence of MoS_2, the enhancement by this dual-element ion implantation process is related to the implanted elements coexisting at

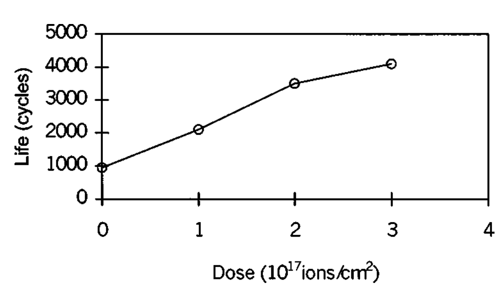

FIG. 3. Friction test lifetime as a function of Mo+S implantation dose.

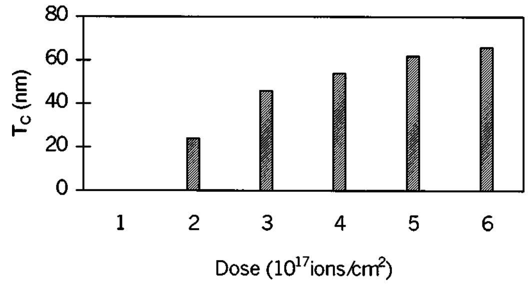

FIG. 4. Computer simulation results of T_C. The implanted ions are Mo+S with a Mo:S ratio of 1:2. The accelerating voltage is 40 kV and $C=0.06$.

the same depth. Using a simulation program developed in our laboratories, we can characterize this dual-element ion implantation process and investigate the effects of high dose, change in target composition, as well as sputtering effects. Some of the parameters of the implantation processing can be calculated and the simulation results are consistent with those obtained from our experiments. The program thus provides a valuable tool for the design and planning of dual ion beam coimplantation processes.

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